SPECIAL RESEARCH PROJECTS

IMS has special research projects supported by national funds. Three projects in progress are:
(a) Chemical Reaction Dynamics
(b) Molecular Photophysics and Science
(c) Novel Material Science

These three projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

(a) Chemical Reaction Dynamics

Folding Mechanism of Protein Molecules Studied by Generalized-Ensemble Algorithms

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Proteins are the most complicated molecules that exist in nature. Since protein structures are closely related to their biological functions, the understanding of their folding mechanism from the first principles is not only very challenging but also very important. To be more specific, it is widely believed that three-dimensional structures of proteins are determined by their amino-acid sequence information. However, nobody has completely succeeded in predicting it solely from the amino-acid-sequence information (prediction from the first principles).

There are two elements for the difficulty. One element is that the inclusion of accurate solvent effects is non-trivial because the number of solvent molecules that have to be taken into account is very large. The other element for the difficulty is that there exist a huge number of local minima in the energy function, and simulations by conventional techniques will necessarily get trapped in one of the local minima without ever finding the energy global minimum. Generalized-ensemble algorithms are new simulation algorithms that can alleviate this second difficulty (for reviews, see Reference 1–3). We have been developing new generalited-ensemble algorithms. We found that the combination of multicanonical algorithm and replica-exchange method is particularly promising.[3)]

The goal of the present project is to further develop and test the effectiveness of generalize-ensemble algorithms in the protein folding problem and to succeed eventually in the prediction of tertiary structures of proteins from the first principles.

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Nonadiabatic Chemical Dynamics

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Quantum reaction dynamics of electronically nonadiabatic chemical reactions have been studied with use of the hyperspherical elliptic coordinate system. These studies have been carried out for DH_2^+ and $O(^1D)HCl$ systems, although the effects of nonadiabatic transitions are not take into account in the latter system. These are important not only by themselves to clarify the quantum dynamics, but also for developing a new semiclassical methodology.[1),2),3)]

The semiclassical TSH (trajectory surface hopping) method for electronically nonadiabatic reactions based on the Zhu-Nakamura theory has been developed and applied to DH_2^+ system. The method has been found to work well compared to the Landau-Zener theory and is expected to be generalized to higher dimensional systems.[4),5)] The similar type of studies are underway for conical intersection systems.

Based on the Teranishi-Nakamura theory to control molecular processes, we have developed a more practically feasible method with use of a sequence of linearly chirped pulses and applied it to selective excitation among closely lying levels and to electronic excitation of a diatomic molecule. Basic analytical theory for the nonadiabatic transition in (t,x) space is being developed, where t is time and x is a spatial coordinate.

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Imaging of Chemical Dynamics

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KATAYANAGI, Hideki; MATSUMOTO, Yoshiteru; NISHIDE, Tatsuhiro; TSUBOUCHI, Masaaki; NISHIZAWA, Kiyoshi

Pump-probe femtosecond photoelectron imaging is employed to observe chemical reactions in isolated molecules and molecular clusters in real time. A pump pulse initiates a reaction and a probe pulse knocks out an electron from a molecule as a function of time delay. Ionization is allowed from any electronic state during the course of a reaction, so this method serves as a versatile means to explore the reaction mechanism. Rotational wave packet motion is utilized to capture the photoelectron angular distribution in the molecular frame that is one of the ultimate quantity to elucidate molecular photoionization dynamics. Photodissociation dynamics is studied by photofragment ion imaging, where vector correlation in the fragment is analyzed in detail to elucidate stereo dynamics. The result is compared with wave packet and classical trajectory calculations on *ab initio* surfaces. Full collision dynamics is studied by using a crossed beam apparatus with an ion imaging detector. Reactive species are produced by photodissociation of precursor molecules, and the scattering distributions of state-selected products are mapped out.

Stereodynamics and Active Control of Chemical Reactions by Using Electrostatic Hexapole State-Selector and Polarized Laser Excitation

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Effect of molecular orientation of a target molecule with respect to a colliding reactant plays a key role in chemical reaction, and this is historically called “steric effect.” It becomes more important for understanding stereodynamics of elementary reactions in the gas phase, in order to control reaction actively. To our knowledge, orientation dependences of “*atom(spnrical)-molecule(vector)*” reactions have been studied using oriented molecules, but the steric effect of “*molecule-(vector)-molecule(vector)*” reaction has not been studied in experiment so far. Typical examples of the “*molecule-molecule*” reaction are the OH + NO and the OH + CO radical reactions. These are our special research project we challenged. Our experimental strategy is to select molecular orientation by use of hexapole state-selector and/or linearly polarized laser. Thus, we have built a new crossed-beam apparatus with a 1-m long hexapole electric field and we have installed a new set of tunable YAG-dye laser system. There are two on-going objectives of our special project as presented in the following.

(1) We investigated the reaction of oriented-OH with aligned-NO. The OH radicals are produced by a dc-discharge of H_2O seeded in He, Ar and Kr. We have developed an intense pulsed beam source and single quantum state $|J\Omega M>$ of OH(X) are selected by a 1-m hexapole field. By probing each *J* state of OH(X) with LIF spectroscopic technique, we could observe the focusing curves for $J = 3/2$ and $5/2$ states. We then state-select their orientation by the hexapole. NO is aligned by the linearly polarized UV laser. The hydrogen atom in the $OH + NO \rightarrow O_2 + H$ reaction and NH product in the $OH + NO \rightarrow NH + O_2$ reaction are detected by REMPI and LIF, respectively. Orientation dependence of the branching ratio of the two reaction channels should provide an insight into details of stereodynamics. Experiment is now being carried out to clarify how molecular orientation affects the branching ratio of production channels.

(2) We proposed a new type of electrostatic state-selector for orienting molecules that consists of seven sets of adjacent hexapole fields to form a honeycomb field for integrating the intensities of seven oriented molecular beam lines. We employed sample gases; Ar, Kr and a polar molecule acetonitrile (CH_3CN, $\mu = 3.92$ D) seeded in those rare gases, to specify the sate-selectivity of the new field. We find that the integrated beam intensity agrees very well with our theoretical estimation, while we can maintain the same beam character of each beam line, such as rotational temperature, stream velocity *etc.* for the integrated beam. We have observed the dependence of the focused CH_3CN beam intensity on the honeycomb electrode voltages, which shows ordinary normal Stark effects, confirming that the present honeycomb-type electrostatic field can be nicely used to state-select and orient molecular beams.

Monte Carlo Simulation of Chemical Gel

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The process of gelation was analyzed by Brownian dynamics simulation using modeled radical polymerization with cross-linkers. Particle densities were set near the gelation threshold determined experimentally (monomer density $d = 200$ mM 400 mM and 600 mM). We performed simulations under two conditions that did (Rule D) and did not (Rule A) prohibit the formation of intra-linkers. With Rule D, we observed gelation at $d = 600$ mM, and clustering at $d = 400$ mM. On the other hand, with Rule A, we did not observe gelation with any of the densities tested. We only observed clustering at $d = 600$ mM. Some quantities were investigated by comparing the results under the two conditions.

Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

KOSUGI, Nobuhiro; HATSUI, Takaki

This project is being carried out at the Beamline 4B of the UVSOR facility. We have three subprojects: (A) spin-orbit, exchange, and molecular field splittings in S 2*p* and P 2*p* excited states, (B) molecules and radicals in condensed phase and in rare gas matrix, and (C) ionic fragmentations following the inner-shell resonance excitation. In (A), we have found some spin-forbidden ionized and excited states in non-radiative (photoelectron emission) and radiative (photon emission) deexcitation spectra in collaboration with the Uppsala University. In (C), we are concentrating on theoretical interpretation of our experimental data measured for last several years.

Computational Study of Quantum Dynamics of a Solute in Solution

OKAZAKI, Susumu; MIURA, Shin-ichi; IWAHASHI, Kensuke; TANAKA, Junji; MIKAMI, Taiji; SATO, Masahiro

Molecular mechanism of vibrational energy relaxation of a solute molecule in solution has been analyzed based upon path integral influence functional theory. Then, solvent normal modes were transformed to each molecular motion in order to examine the couplings in terms of solvent molecules. Coupling which has large contribution to the relaxation could be attributed to a particular water molecule. Mixed quantum-classical molecular dynamics method has also been applied to the analysis of dynamic aspects of the coupling. Component which is resonant with the solute wave function was extracted from the solute-solvent interaction $<0|V|1>$. In a short time-scale, *i.e.* sub ps, it shows almost random behavior. However, in longer time-scale, ~ ps, it clearly shows relaxation.

Simulation method for quantum liquids has been investigated, too. A new hybrid Monte Carlo method has been developed to simulate liquid helium in super fluid state.

Photodissociation of 16 Valence Electron Systems, OCS and N_2O

NANBU, Shinkoh; MINAMINO, Satoshi; MAKI, Jun; AOYAGI, Mutsumi

OCS and N_2O molecules have similar characters for the low-lying electronic states, because both molecules are characterized with the 16 valence electron system, and that is the reason why the electronic structures are assigned to $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ symmetries in $C_{\infty v}$. And also, we can have an image of forming the similar features for the PESs of OCS and N_2O, and furthermore having the similar dynamics for the photodissociation processes, $OCS + h\nu \rightarrow CO(^1\Sigma^+) + S(^1D)$ and $N_2O + h\nu \rightarrow N_2(^1\Sigma_g^+) + O(^1D)$. Therefore, we began to study the photodissociation process with OCS, collaborating with Prof. Suzuki's group. First, the speed, angular, and alignment distributions of S atoms from the ultraviolet photodissociation have been measured by a photofragment imaging technique. From the excitation wavelength dependence of the scattering distribution of S, the excited states accessed by photoabsorption were assigned to the A' Renner-Teller component of the $^1\Delta$ and the A"($^1\Sigma^-$) states. It was found that the dissociation from the A' state gives rise to high- and low-speed fragments, while the A" state only provides the high-speed fragment. In order to examine the bimodal speed distribution of S atoms, two-dimensional PESs of OCS and non-adiabatic coupling elements were calculated with ab initio MO CI method, fixing the CO bond distance, and wave packet dynamics were performed including the non-adiabatic transitions. The theoretical results could qualitatively reproduce the experimental feature. However, they could not quantitatively agree with the measurements. In the present work, wave packet dynamics were performed to study the similarity due to the same 16 valence electron systems, using the newly determined three-dimensional PESs for OCS and N_2O.

Development of Single-Molecule Physiology

KINOSITA, Kazuhiko, Jr.

Our effort in this year was to establish a new lab in the newly built building of the Center for Integrative Bioscience. Our lab aims at single-molecule physiology, where we watch and manipulate individual protein/RNA molecules (molecular machines) under an optical microscope to elucidate their functions (see Research Activities). The microscopes need to be in a dust-free environment at a controlled temperature. For this purpose, we designed special chambers that would keep the sample temperature to within ± 0.1 ˚C. We also developed stable microscope stages and a beam homogenizer with little vibration. Software for image analysis is also being developed. I hope we are now ready for a new start.

Ultrafast Protein Dynamics Probed by Time-Resolved Resonance Raman Spectroscopy

KITAGAWA, Teizo

Ultrafast protein dynamics were examined with myoglobin (Mb) using picosecond time-resolved resonance Raman spectroscopy with a stress on structural changes and vibrational energy relaxation of heme. Studies on the structural relaxation of Mb following CO photolysis revealed that the structural change of heme itself (core expansion), caused by CO photodissociation, is completed within the instrumental response time of the time-resolved resonance Raman apparatus used (~ 2 ps). In contrast, changes in the intensity and frequency of the iron-histidine (Fe–His) stretching mode upon dissociation of the trans ligand were found to occur in the picosecond regime. The Fe–His stretching band is absent for the CO-bound form, and its appearance upon photodissociation was not instantaneous, in contrast with that observed in the vibrational modes of heme, suggesting appreciable time evolution of the Fe displacement from the heme plane. The intensity reflected the out-of-plane displacement of iron, and 80% of the movement occurred in 2 ps but the remaining 20% occurred in 40 ps. The band position of the Fe–His stretching mode changed with a time constant of about 100 ps, indicating that tertiary structural changes of the protein occurred in a 100-ps range. This rate was dependent on viscosity of solvent ($k = \eta^{-0.3}$), indicating that the small change at the Fe–His bond is communicated to the protein surface through a conformation change, and conversely the change of Fe–His bond is controlled by the surface of the protein. Temporal changes of the aniti-Stokes Raman intensity of the ν_4 and ν_7 bands demonstrated immediate generation of vibrationally excited heme upon the photodissociation and successive decay of excited populations, whose time constants were 1.1 ± 0.6 and 1.9 ± 0.6 ps, respectively. This technique has been applied to identify an axial residue of a sensor protein, CooA, for which geminate recombination of photodissociated CO is very fast ($\tau = 70$ ps) and therefore the Fe–His (His77) stretching Raman band could be detected only transiently with this technique.

(b) Molecular Photophysics and Science

Development of Dynamic Spectroscopy Apparatus Having Nanometer Spatial Resolution

IMURA, Kohei; NAGAHARA, Tetsuhiko; OKAMOTO, Hiromi

Recent remarkable technological progress in scanning near-field optical microscope (SNOM) has made it possible to perform optical measurements with very high spatial resolution beyond the diffraction limit. We are constructing an apparatus for space- and time-resolved spectroscopic measurements, by combining SNOM and ultrafast time-resolved technique. With this apparatus, we have achieved ~ 100 nm spatial and ~ 100 fs temporal resolution at the same time. Various photophysical phenomena probed under such extremely high space and time resolution can be of considerable significance not only in physics and chemistry but also in biology, and thus will open a new research activity. We plan to make use of this experimental methodology to investigate basic problems on chemical processes of mesoscopic systems. This technique also has a potential to shed a new light on nanoscale material science.

Experimental setup is schematically depicted in Figure 1. An apertured fiber probe is used to obtain spatial resolution of better than 100 nm. Radiation from a femtosecond Ti:sapphire laser or other pulsed or cw lasers are used as an excitation light source. The sample is irradiated through the fiber probe. The emission from the sample is collected through the same fiber probe tip or collected by a separate far-field optics. The preliminary experimental results are reported in II-A.

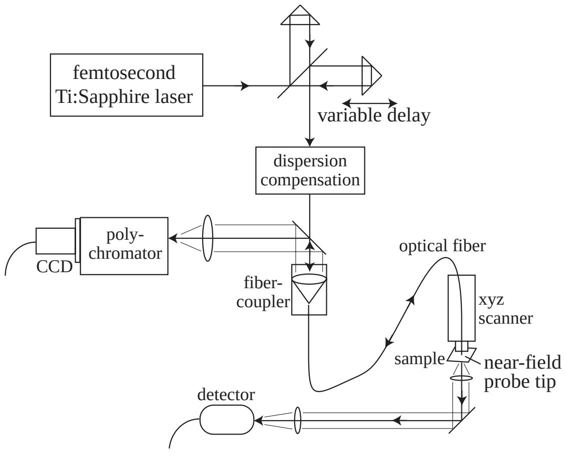

Figure 1. Schematic diagram of the experimental apparatus.

(1) Laser Cooling and Trapping of Metastable Helium Atoms
(2) Laser Spectroscopic Studies of Atoms and Ions in Liquid Helium

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In studies on "laser cooling and trapping of metastable helium atoms," we have been still constructing a new laser trapping apparatus for realizing the Bose-Einstein condensation of metastable He atoms. In the new apparatus, the metastable atomic beam is tightly collimated with a corner cube prism chain of totally 30 cm long, and deflected by an angle of 30 degrees after some deceleration in order to prevent the intense ground state beam from attacking the trapping region (see II-B-1). On the other hand, in "laser spectroscopic studies of atoms and ions in liquid helium," we have experimentally observed some interesting differences between excitation spectra of Eu atoms in liquid ^{4}He and ^{3}He: sharp zero phonon lines and phonon side bands have been seen for both liquid ^{4}He and ^{3}He, but additional bands have been seen only for ^{4}He. These bands can be roton or maxon spectra of liquid ^{4}He, in which the dispersion relation is well determined, but detailed investigation is now in progress (see II-C-1).

Structure, Relaxation and Control of Reactive Cluster Studied by Two-Color Laser Spectroscopy

FUJII, Masaaki

A molecular cluster is a microscopic system of solution and/or crystal, and is thought to provide detailed information on relaxation and reaction dynamics in condensed phase. However the molecular clusters which have been studied are mainly static system which has no reaction pathway after photo-excitation, and consequently spectroscopic information which concerns the reaction mechanism has not been obtained sufficiently. In this research project started from 2000, we will apply various laser spectroscopy to the reactive clusters to reveal detailed mechanism of intracluster reaction. The originally developed spectroscopies, such as nonresonant ionization detected IR spectroscopy, UV-IR-UV ion dip spectroscopy, and the picosecond time-resolved IR dip spectroscopy, are described in the Research Activities of this group. By using these method, we have measured the IR spectra of solvated clusters, such as phenol/ammonia , naphthol/water and alcohol, carbazole/water and 7-azaindole dimers, and have discussed the relation between the structure and intracluster reactions. (see Research Activity III-E "Spectroscopy and Dynamics of Vibrationally Excited Molecules and Clusters" for detail)

Dynamics of Molecular Superexcited States Studied by Electron and Fluorescence Spectroscopy

MITSUKE, Koichiro

One of our main interests is to elucidate the spectroscopy and dynamics of molecular superexcited states. Though these states often play crucial role in photoexcitation and bimolecular reactions in the VUV and soft X-ray regions, the knowledge of their characteristics is very limited. Owing to autoionization in a very short period and strong perturbation from neighboring neutral states, superexcited states experience various decay pathways such as neutral dissociation, internal conversion, and intramolecular vibrational redistribution. We have employed three experimental methods which serve as a means of providing insights into such processes: Photoelectron spectroscopy, dispersed fluorescence spectroscopy, and laser induced fluorescence spectroscopy. Taking maximum advantage of the tunability of synchrotron radiation, we have obtained hundreds of spectra at different primary photon energies. Assembling and comparing these one-dimensional spectra enable us to uncover novel decay pathways. For example, superexcited states are often subject to neutral dissociation into electronically excited fragments. These fragments release their internal energy by emitting fluorescence. Dispersed fluorescence spectroscopy is helpful for us in assigning the dissociation products and determining their vibrational distribution. However, this is not sufficient. If we wish to decide on which precursor state gives rise to the fragments, we should carry on excitation spectroscopy for the particular emission band with changing the primary photon energy. Namely, the fluorescence intensity should be measured as a function of two variables, the initial synchrotron radiation photon energy and final fluorescence wavelength. Two-dimensional plots thus obtained allow us to investigate involved dissociation mechanism of a superexcited state, to evaluate the magnitudes of the electronic coupling with other neutral or ionic states, and to achieve description on the potential energy surface of the relevant dissociative state.

Decay and Dissociation Dynamics of Core Excited Molecules

SHIGEMASA, Eiji; GEJO, Tatsuo

Thanks to the high performance of the newly constructed Varied-Line-Spacing Plane Grating Monochromator (VLS-PGM) at BL4B of the UVSOR facility, various spectroscopic investigations on molecular core-levels with high-resolution have became feasible. The dynamics of molecular inner-shell excitation and relaxation processes is complex even for simple molecules, and thus it is advantageous to use various experimental techniques together with such a high performance monochromator in the soft x-ray region.

The construction of apparatuses for two different types of electron-ion coincidence experiments has been started. A high luminosity double toroidal analyzer (DTA) equipped with a two-dimensional detector makes it possible to measure the angular distribution and kinetic energy of electrons/ions simultaneously. Owing to unexpected short-circuits in the electrical wiring for DTA, performance tests on it has been delayed. Threshold electron spectroscopy has proved to be very powerful in the investigation of electron correlation phenomena not only in atoms but also in molecules. In the angle-resolved photoion spectroscopy applied to the inner-shell excitations of linear molecules, the parallel and perpendicular transitions are distinguishable. Thus, it is expected that the combination between a threshold electron spectrometer and an angle-resolved photoion spectrometer can provide a rare opportunity to obtain threshold electron spectra including the symmetry information on the excited states, which can be called as symmetry-resolved threshold electron spectra. It has been confirmed through the test experiments using VLS-PGM that the symmetry-resolved threshold electron spectra for N_2 can be measured, although the signal intensity under high-resolution condition was considerably low.

A new project towards the practical usability of the free electron laser (FEL) developed at UVSOR has been initiated in 2000. Two-photon double-resonant excitation spectrum of the autoionization Xe* $5p^5 4f$ resonance *via* the Xe* $5p^5 5d$ intermediate state has been successfully derived. Though similar experiments in a shorter wavelength region for FEL have been attempted, unknown strong backgrounds observed in the photoion detection system have prevented us from measuring the corresponding spectrum. A detailed inspection of the whole experimental setup is in progress.

(c) Novel Material Science

Calculations of Large Molecular Systems

ISHIMURA, Kazuya; NAGASE, Shigeru

In material science, it is of increasing interest to make reliable calculations on large molecular systems using ab initio molecular orbital or density functional methods. For this purpose, high-performance parallel calculations on PC clusters are investigated by developing computer network and effective parallel programs. Up to now, relatively good cost and speed performance are obtained.

Response of Protein Conformation to Pressure: Theoretical Study on Partial Molar Volume

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Protein conformation in solution is fluctuating around its equilibrium structure, and the occurence of the structural fluctuation is governed by its free energy. It has recently been demonstrated by Akasaka and his coworkers that pressure can be an impeccable thermodynamic parameter to realize structural fluctuations occuring in protein. Using pressure as an order parameter, Aksaka could have detected a set of NMR chemical shifts corresponding to a variety of conformations, from native to completely random states, which are supposedly the hierarchical substates appearing in the protein in the ambient condition. Since occurence of a substate of protein with higher free energy is rare, it is difficult to detect such event by usual methods such as spectroscopy.

The thermodynamic response of protein conformation to pressure is manifested in its partial molar volume (PMV), due to the Le'Chaterier law. It is, therefore, essential to analyze PMV in order to understand conformational fluctuation of protein. The theoretical analysis of PMV is of particular importance in this respect, because there is no way to measure experimentally PMV of individual substates. If one is able to calculate PMV with theoretical method, it is not difficult task to obtain PMV of a substate of protein by producing such a conformation by, say, the multi-cannonical Monte-Carlo sampling coupled with the RISM theory.

Recently, we have developped a method to calculate PMV of biomolecules in aqueous solution by combining the RISM/3D-RISM with the Kirkwood-Buff theory. In the special research project, we have carried out the theoretical treatment for PMV of a series of amino acids. The results for the twenty amino acids are not only in quantitative agreement with the experiments, but also able to discriminate the specificity each amino acid manifests in PMV.

We have also calculate the partial molar volumes and their changes associated with the coil(extended)-to-helix transition of two types of peptide, glycine oligomer and glutamic acid oligomer, in aqueous solutions by using the Kirkwood-Buff solution theory coupled with the three-dimensional reference interaction site model (3D-RISM) theory. The calculated volume change upon the transition turn out to be small and positive in accord the experiment. The volume is analyzed by decomposing it into five contributions following the procedure proposed by Chalikian and Breslauer: the ideal volume, the van der Waals volume, the void volume, the thermal volume, and the interaction volume. The ideal volumes and the van der Waals volumes do not change appreciably upon the transition. In the both cases of glycine peptide and glutamic acid peptide, the changes in the void volumes are positive, while those in the thermal volumes are negative, and tend to balance those in the void volumes. The change in the interaction volume of glycine-peptide does not significantly contribute, while that of glutamic acid-peptide makes negative contribution.

Theory for Equilibrium and Non-Equilibrium Properties of Low-Dimensional Molecular Materials with Strong Electron Correlation

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In low-dimensional molecular materials, electron correlations are essential for the understanding of novel electronic phases. i) Mixed-stack organic charge-transfer complexes have columns of alternating donor and acceptor molecules. Neutral-ionic and dimerization phase transitions are observed in them. Since the dimerization was observed in some neutral compounds, importance of the long-range Coulomb interaction has been pointed out. We have demonstrated by the finite-temperature density-matrix renormalization-group method that transfer-modulating electron-lattice coupling also brings about dimerization in the neutral phase and that the transition becomes continuous then. The TTF-CA complex shows the discontinuous and simultaneous, neutral-ionic and dimerization phase transitions. It shows the photoinduced phase transition as well. We have solved the time-dependent Schrödinger equation to reproduce peculiarities found in time-resolved spectroscopy, such as a) the threshold intensity above which the transition takes place, b) the macroscopic coherent oscillations of neutral-ionic phase boundaries, and c) the quick loss of the second-harmonic-generation signal. ii) Among halogen-bridged binuclear metal complexes, binuclear platinum complexes are synthesized and investigated extensively. They show a variety of electronic phases owing to competing kinetic energy, Coulomb repulsion, and electron-lattice coupling. When the ligand is pop, electrons are so localized that the perturbation theory from the strong-coupling limit works very well for the ground and optically excited states. When the halogen is iodine in addition, as the distance between the neighboring MM units increases by changing counter ions or by reducing pressure, a discontinuous transition takes place from the charge-density-wave phase to the charge-polarization phase. This can be explained by decreasing electron-lattice coupling strength compared with repulsion strength. In those materials which show the pressure-induced transition, a photo-induced transition is observed in the hysteresis loop. The transition is, however, only from the charge-density-wave to charge-polarization phases. We have clarified its mechanism. a) The lowest-energy photoexcitation brings about inter-unit charge transfer only in the former phase. b) The high-energy photoexcitation in the latter phase transfers charge so locally that the former phase never proliferates like a domino effect. iii) The dimensional crossover in excitation spectra is demonstrated by the finite-temperature density-matrix renormalization-group method. At a particular band filling that is common in organic conductors, electron correlation is so strong in the most conducting direction that electron motion is confined in this direction. The perpendicular motion takes place only incoherently. This explains the observed behavior that is reminiscent of the doped Mott insulators.

UHV System for MOKE Measurements

YOKOYAMA, Toshihiko; NAKAGAWA, Takeshi

The magnetoptical Kerr effect (MOKE) is usually the most suitable method to characterize magnetic properties of ultrathin films since the rotation angle of the electric-field vector of linearly polarized lights is nearly proportional to the magnetization of the films. Although we are planning to use x-ray magnetic circular dichroism (XMCD) in UVSOR, in-laboratory experiments is also important for several reasons. First, detailed and time-consuming characterization is required especially for the preparation of new magnetic materials. Since the beamtime in UVSOR is limited, some in-laboratory equipment is essential. Second, the measurements in the applied magnetic field is easier in MOKE since MOKE detects polarization of the reflected lights while XMCD scales emitted electrons.

We are thus constructing a new ultrahigh vacuum (UHV, $< 1 \times 10^{-8}$ Pa) system in which *in situ* MOKE can be measured. The system contains a standard UHV pumping unit, a surface cleaning system of sputtering and annealing of substrates, and a molecular beam epitaxy (MBE) system. The substrate can be cooled down to ~ 100 K using liquid nitrogen and to ~ 25 K using liquid He. A magnetic field can be applied to samples in UHV with a simple electromagnet up to 3000 Gauss. The magnetic field is not so large but is usually sufficient for ultrathin films of 3*d* elements. Both the polar MOKE geometry for perpendicular magnetization and the longitudinal MOKE for in-plane magnetization are available.

Using the UHV MOKE system, we will investigate magnetic properties of ultrathin metal films, nanowires and nanodots, especially control of magnetism using surface chemical techniques such as gas deposition.

Pulsed Methods of Electron Spin Resonance Spectyroscopy

KATO, Tatsuhisa; FURUKAWA, Ko

Electron spin resonance (ESR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of ESR spectroscopy enables us to investigate the transient phenomena in detail. The pulsed ESR spectroscopy gives us the prototyped demonstration of the time-dependent spectroscopy. Some time-dependent measurements were experimentally performed and compared with the theoretical model calculation. The advanced ESR method was applied to the study on the high spin state of Gd@C_{82} described in section II-J-1 and of multi-cations of aromatic amines in section II-J-2, and to the study on the reaction mechanism in the reduction of metallofullerenes by solvation in section II-I-3.

Spectroscopic Studies of Organic Conductors

YAKUSHI, Kyuya

The low-frequency reflectivity of an organic conductor provides us with a wealth of information on the nature of charge carriers. For instance, the anisotropy of a band structure, bandwidth, effect of electron-electron correlation, and electron-molecular vibration (EMV) coupling parameters can be extracted from the analysis of the reflectivity or optical conductivity curve. For this subject, we have studied charge-transfer salts of EDOEDT-TTF, $(\mathrm{BDTFP})_2X(\mathrm{PhCl})_{0.5}$, $(\mathrm{EO\text{-}TTP})_2\mathrm{AsF}_6$. In relation to this subject, we have conducted the quantum chemical study of NiPc, NiPc^+, CoPc, and CoPc^+. We could reproduce the intensity of the diagnostic vibrational bands, which characterize the oxidation state of NiPc and CoPc. The ring oxidation in CoPc^+ is also very well reproduced by this calculation. This calculation including the overlap integral between the one-dimensional conductor, $\mathrm{CoPc(AsF_6)_{0.5}}$, is consistent with the characteristic magnetic properties obtained by the experiment of dilute alloy with $\mathrm{NiPc(AsF_6)_{0.5}}$.

Usually the molecular vibrations (local phonons) are screened by strong electronic absorption by charge carriers, and thus very few optical phonons are detected in the reflection spectrum. In this sense, Raman spectroscopy is a powerful method complementary to reflection spectroscopy for understanding molecular vibrations in a metallic state. Since some molecules have charge-sensitive vibrational modes, the Raman spectroscopic method is a powerful tool to detect the site-charge distribution (oxidation state of molecule). We are investigating the charge ordering (CO) phenomena in organic conductors using the technique of infrared and Raman spectroscopy. In the organic charge-transfer salts, CO is originated from the localization of charge carriers. Since the charge carriers in organic crystal is located at the boundary between localized and extended (delocalized) states, CO is widely found through the phase transition. The interest in CO is quickly growing, since CO is theoretically considered as being related to the charge-fluctuation-mediated superconducting mechanism. As to this subject, we have thoroughly studied the vibrational spectrum of θ-(BEDT-TTF)$_2$Rb-Zn(SCN)$_4$ using polarized Raman and infrared spectroscopy with the aid of ^{13}C-substitued isotope compound. For θ-(BDT-TTP)$_2$Cu(NCS)$_2$, We have extended the study on CO to the following charge-transfer salts, θ-(BDT-TTP)$_2$Cu(NCS)$_2$, (Me$_2$-DCNQI)$_2$Cu$_x$Li$_{1-x}$ ($0 < x < 1$), and (DI-DCNQI)$_2$*M* (*M* = Ag, Li, Cu).

Broad-Line Solid State NMR Investigation of Electronic States in Molecular-Based Conductors

NAKAMURA, Toshikazu; FUJIYAMA, Shigeki

Molecular based conductors are one of the extensively studied materials. Their fundamental properties have been very well clarified. The development of the understanding of the electronic phases of these materials enables us systematic investigations of low-dimensional highly correlated electrons systems. For example, recent progress of the investigation for the charge ordering and/or charge disproportionation states in quasi-two-dimensional organic conductors, θ-type BEDT-TTF compounds, are attracting much attention in the field of solid state physics. As for quasi-one-dimensional systems, (TMTTF)$_2$*X*, have been extensively studied so far because of their various ground states such as spin-Peierls, AF, IC-SDW and superconductivity. Moreover the origin of the paramagnetic insulating states is an open question. To investigate the low temperature electronic phases, we synthesized ^{13}C substituted TMTTF molecules; the two central carbon sites, of which hyperfine coupling constants are much larger than those of hydrogen sites, have been labeled with ^{13}C. We investigated the charge configurations and spin dynamics in the low temperature phases of (TMTTF)$_2$*X*.

Broad-Line Solid State NMR is a powerful microscopic investigation; they are advantageous for studying the fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Competition of the electronic phases in molecular based conductors has attracted much attention. Investigation of such electronic phases in molecular based conductors is important to understand the unsolved fundamental problems in the field of solid state physics. The aim of this project is to clarify the electronic state (charges and spins) of molecular based compounds by microscopic point of view.

In this project, we are preparing a new NMR system under ultra-low temperatures to study more detailed electronic structure from microscopic points of view. We also try to carry out experiments with new devices under unconventional circumstance.

The following projects are also now going on.

[1] Investigation of charge ordering States in (TMTTF)$_2$*X*
[2] Charge and spin dynamics in organic conductors
[3] ^{13}C NMR study of two-component spins system, (BEDT-TTF)-TCNQ
[4] Low temperature electronic phases in (EDT-TTF)$_2$*X*

Development of New Organic Conductors

KOBAYASHI, Hayao; FUJIWARA, Hideki; TANAKA, Hisashi; ZHANG, Bin; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

In order to make contribution to the progress of solid state chemistry and physics of molecular materials, we have tried to develop new types of molecular conductors and examin their physical properties. The main results obtained in the last one year are as follows. (1) We have recently reported the first example of single-component molecular metal based on the transition metal complex molecule Ni(tmdt)$_2$. For the development of single-component molecular metal, it is of key importance to design “anomalous π molecule” with very small HOMO-LUMO gap (< 0.5 eV) and TTF skeleton permitting to produce the sufficiently large intermolecular multi-dimensional HOMO-HOMO and LUMO-LUMO interactions. Since the single-component molecular metals have been already realized, one of the next targets may be the magnetic molecular metal based on the single-component molecules with the magnetic transition metal ions such as Cu^{2+} and Co^{2+}. If the molecule has a localized magnetic moment on the central atom and the intermolecular magnetic interaction is mediated by the π conduction electrons, the large intermolecular magnetic interaction can be expected. We have recently found that the conduction electron and magnetic moments coexist in the crystal of [Cu(dmdt)$_2$]. (2) Under the collaboration with Dr. Uji, we found the field-induced superconductivity of λ-BETS$_2$FeCl$_4$ in 2001. Very recently, we have discovered the second example of the organic conductor exhibiting field-induced superconducting transition through the examination of the magnetoresistance of κ-BETS$_2$FeBr$_4$ up to 15 T and down to 0.58 K. These findings seem to suggest the field-induced superconductivity, which is a very rare phenomenon in inorganic conductor, can be observed in many two-dimensional magnetic organic superconductor with antiferromagnetic interaction between π conduction electrons and localized magnetic moments. (3) For the realization of molecular electronic devices, it will be necessary to develop “dual-action systems” whose conducting properties can be sharply controlled by external forces. One of the possible dual-action molecular systems will be a composite system consisting of organic layers responsible for electron conduction and inorganic layers with localized magnetic moments, whose conductivity can be controlled by tuning magnetic state of the inorganic layers. We have recently reported the first example of the novel dual-functional magnetic organic conductor whose superconducting state can be sharply switched on or off by controlling the metamagnetic transition of the anion layers.

Design and Synthesis of Organic Spin-Ladder Systems

HOSOKOSHI, Yuko; KATOH, Keiichi; INOUE, Katsuya

The magnetic properties on the low-dimensional quantum spin system with an energy gap have attracted great interests in recent years. Especially the antiferromagnetic S = 1/2 spin ladder system draws much attention, since it is interesting in terms of the Haldane state and the high T_C superconductivity. The ground state of the S = 1/2 ladder is the resonating valence bond (RVB) state or the dimerized state. The property of the S = 1 antiferromagnetic ladder is also interesting. For the ground state, the Haldane state or the dimer state is expected.

Here we present organic spin ladder systems. We employed *N-tert*-butyl aminoxyl as a spin source of S = 1/2, focusing on the stability, crystallinity and controllability of the crystal structure. We must mention that the electrostatic energy plays substantial role in controlling the molecular packing of the neutral organic crystal. The partial charges on the oxygen and nitrogen atoms on the aminoxyl group prefer the intermolecular contacts between the aminoxyl groups. We use the intermolecular interactions between the aminoxyl groups as an antiferromagnetic leg. As an antiferromagnetic rung, we combine two S = 1/2 spins by intramolecular antiferro-magnetic exchange coupling. As for the S = 1 ladder, we employed *m*-phenylenebis(*N-tert*-butylaminoxyl), BNO, as an S = 1 unit. Intramolecular exchange coupling in BNO is reported to be $2J/k_B$ ~ 600 K. Although there are several examples of S = 1/2 two-leg ladders, BIP-BNO (BIP-BNO = 3,5'-bis(*N-tert*-butylaminoxyl)-3',5'-dibromobiphenyl) is the first example of the genuine organic system, which consists only of light elements and is ideal Heisenberg spin system. As far as the authors know, there are no example of the S = 1 ladder compound. The crystals of BIP-TENO (3,3',5,5'-tetrakis(*N-tert*-butyl-aminoxyl)-biphenyl) form an antiferromagnetic double spin chain composed of spin dimers, in which two spins are coupled ferromagnetically. When the dimer is taken as an unit, this system can be regarded as an S = 1 ladder. (see V-C)

Construction of BL-7A at UVSOR for STM Observation of SR Irradiation Induced Photochemical Reaction on Si Surfaces

NONOGAKI, Youichi; URISU, Tsuneo

This beamline is constructed for STM observation of surface photochemical reaction induced by illumination of undulator radiation. The surfaces are exposed to high flux quasi-monochromatic light with varying photon energy generated by the undulator. We have been interested in photo-stimulated desorption of SiO_2 on Si surfaces due to the application of nano-fabrication by using undulator radiation.

Using bending magnet radiation, we have done many experiments of SR stimulated desorption of SiO_2. To avoid the reduction of photon flux, the bending magnet radiation was not monochromatized. We have found that Si (111) 7×7 reconstructed surfaces appears after 2 h irradiation of SiO_2 covered Si surface even at low temperature of 700 °C. It indicates that SiO_2 desorbed completely by SR irradiation effects.

To investigate reaction mechanism of the photo-stimulated desorption of SiO_2 was an attractive target. It is necessary to observe the Si surfaces after irradiation of various excitation photon energies. Since monochromatic light from bending magnet radiation is too weak, undulator radiation should be needed.

Now, we prepare construction of new BL-7A undulator beamline, which includes a plane and a toroidal mirrors as optical components. The plane mirror is used for branching the beamline and the toroidal mirror for focusing and adjusting spot position. The STM system was replaced in December 2001, which was designed so that the SR beam can illuminate the sample surface under the STM tip. Therefore, sample surfaces are observed just after the SR illumination without the sample transfer. By upgrading the beamline and the STM system, we will obtain deep knowledge about relationship between SiO_2 photo-stimulated desorption and Si core-electron transition.

Catalytic Oxidation of Alcohols in Water under Atmospheric Oxygen by Use of an Amphiphilic Resin-Dispersion of Nano-Palladium Catalyst

UOZUMI, Yasuhiro

We have previously reported that amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported palladium-phosphine complexes catalyzed various palladium-mediated reactions smoothly in water. These observations prompted us to design and prepare the PS-PEG resin-supported palladium nanoparticles, which should have high catalytic activity owing to the large surface area of the nanoparticles and water-based reactivity provided by the amphiphilicity of the PS-PEG matrix combined in one system. Catalytic alcohol oxidation was achieved in water under atmospheric pressure of molecular oxygen by use of amphiphilic polymer-supported palladium nanoparticles.

An amphiphilic resin-dispersion of palladium nanoparticles was readily prepared by reduction of a PS-PEG resin-supported palladium(II) complex. Thus, a chelating ligand anchored on PS-PEG amino-resin was complexed to palladium by treatment with an equimolar amount of $Pd(OAc)_2$ to give the stable 16-electron divalent palladium complex. The complex was treated with benzyl alcohol in refluxing water to give the desired amphiphilic PS-PEG resin-dispersion of palladium nanoparticles. Transmission electron microscopy (TEM) of the resulting palladium-resin shows that the palladium particles have a mean diameter of 9.1 nm with a narrow size distribution. The amphiphilic resin-dispersion of palladium nanoparticles exhibited high catalytic activity in aerobic oxidation of alcohols in water.

Reductive Activation of Carbon Dioxide and Oxidative Activation of Water Aimed at Energy Conversion

TANAKA, Koji

Multi-electron reduction of CO_2 affording organic compounds is much more important than two-electron reduction of CO_2 producing CO and/or HCOOH, because of the continuous decrease of free energy changes with an increase of the number of electrons participated in the reduction. Taking into account that CO_2 is smoothly converted to CO on metal complexes through metal-η^1-CO_2 ones, the principal factor to achieve multi-electron reduction of CO_2 is reduction of M–CO bonds without accompanying reductive cleavages of M–CO bonds due to accumulation of too much electrons in the central metals. A catalytic system, which can supply electrons to M–CO bonds through ligand localized redox reactions, may realize reduction of the M–CO bonds without evolving CO under protic conditions. Some Ru-CO complexes with mono-dentate 1,8-naphthyridine easily form a five-membered metallacycle by an attack of free nitrogen to the carbonyl carbon when the ligand undergoes one-electron reduction. We, therefore, examine the reactivity of a variety of metal-naphytylidine complexes aiming at multi-electron reduction of CO_2.

Reactivity of high valent metal-*oxo* complexes is of current interest from the viewpoints of the enzymatic activation of dioxygen on metals and oxidation or oxygenation of organics such as P-450 enzymes. Mechanistic understandings of the reactivity of O_2 on metals have, however, been limited because of the difficulty of selective cleavage of the O–O bond of O_2 on metals in artificial systems. Oxidation of Ru-OH_2 complexes causes simulataneous loss of protons to form high-valent Ru=O ones, which attract much attention to elucidate the reactivity of metal-*oxo* frameworks. Quinone is electrochemically non-innocent ligand and undergoes stepwise reduction to yield semiquinone and catecholate. Taking into account that higher oxidation states of Ru=O complexes have been obtained by sequential electron and proton loss of Ru-OH_2 ones, introduction of quinone ligands as an electron acceptor into the Ru-OH_2 framework would induce deprotonation of the aqua ligand instead of the oxidation of the central Ru ion. Along the line, we have prepared a series of metal-aqua complexes with dioxolene aimed at the smooth conversion from the aqua to hydroxy and *oxo* ligands.

Coordination Chemistry of New Multidentate Ligands and Activation of Small Molecules

KAWAGUCHI, Hiroyuki; MATSUO, Tsukasa

The efficient activation of dinitrogen under mild conditions is a challenging topic in chemistry due to its important application. Although dinitrogen complexes of almost transition metals have been prepared, there are few examples of well characterized transition metal compounds which are capable of cleaving the N≡N triple bond. As part of a research program aimed at developing new ancillary ligands to support reactive metal centers, we have found it attractive to utilize linked aryloxide ligands, in which aryloxide units are connected at *ortho* positions through methylene linkers. One of the advantages of this system is the flexible coordination modes, and the trimer can be coordinated in a U- and an S-conformation. In addition, there is the opportunity for coordinative unsaturation as compared to the calix[4]arenes. In this scenario, we have prepared titanium and niobium complexes supported by linked aryloxide trimers. In the case of niobium complexes, we found that the N≡N triple bond split took place in a mild condition. Further study to isolate an intermediate during the course of this reaction is currently underwent.

Developments and Researches of New Laser Materials

SARUKURA, Nobuhiko; OHTAKE, Hideyuki; KOZEKI, Toshimasa; ONO, Shingo[1]
([1]Tokyo Univ. Sci.)

Although development of lasers is remarkable, there are no lasers which lase in ultraviolet and far infrared regions. However, it is expected that these kinds of lasers break out a great revolution in not only the molecular science but also in the industrial world.

In this project we research characters of new materials for ultraviolet and far infrared lasers, and develop new lasers by using these laser materials.

Development and Research of Advanced Tunable Solid State Lasers

TAIRA, Takunori; SHOJI, Ichiro; PAVEL, Nicolaie; DASCALU, Traian; ISHIZUKI, Hideki; SATO, Yoichi; SAIKAWA, Jiro

The use of diode lasers to pump solid-state lasers opens new horizon in laser science. Diode-pumped solid-state lasers are compact, reliable, and efficient sources of coherent radiation. They can provide excellent spatial mode quality and narrow linewidths. The high spectral power brightness of these lasers has allowed high efficiency frequency extension by nonlinear frequency conversion. Moreover, the availability of new and improved nonlinear optical crystals makes these techniques more practical. Recently attention has been directed to the trivalent ytterbium ion doped YAG. The advantages of Yb:YAG lasers for a high power, high stability and wide tunability laser operation are well recognized due to its small quantum defect, long upper-state life time and wide gain width.

On the other hand, quasi phase matching (QPM) is a new technique instead of conventional birefringent phase matching for compensating phase velocity dispersion in frequency conversion. Inasmuch as the pool of mature nonlinear optical materials is limited and development of new materials takes time and cost, QPM is a useful method for extending the range of available nonlinear optical materials. The ability to pattern a QPM structure allows the nonlinear materials to be engineered for desired interactions, meaning molecular-science-specified lasers are obtainable through these artificial materials.

In this projects we research and develop new diode-pumped-solid-sate lasers and new frequency conversion devices. Especially, we will focus on the combination of microchip lasers and QPM devices. These kinds of advanced tunable solid-state light, so to speak "Chroma-Chip Lasers," will assist the research of molecular science.

Synthesis of Oligonaphthalenes and Oligoanthracenes and Applications for Organic Field-Effect Transistors

ITO, Kaname; SAKAMOTO, Youichi; SUZUKI, Toshiyasu

We have synthesized 2,6-ternaphthalene (**3N**) and 2,6-quaternaphthalene (**4N**). These oligomers are colorless crystalline solids, which showed sharp melting endotherms at 287 and 351 °C, respectively. **3N** is slightly soluble in some solvents, but **4N** is insoluble in common organic solvents. 2,6-Bianthryl (**2A**) and 2,6-teranthracene (**3A**) were also synthesized by the Suzuki coupling. These oligomers are bright yellow crystalline solids, which showed sharp melting endotherms at 365 and 491 °C, respectively. **2A** and **3A** is insoluble in common organic solvents. OFETs were fabricated using anthracene oligomers as the *p*-type semiconductors. They showed the field effect with hole mobilities in the range of 10^{-3}–10^{-2} cm^2/Vs.

Field Effect Transistors of BTQBT and Its Derivatives

TAKADA, Masaki[1]; YAMASHITA, Yoshiro[2]; TADA, Hirokazu
([1]GUAS; [2]Tokyo Inst. Tech.)

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Field effect transistors (FETs) using organic semiconductor thin films as active layers have been studied intensively because they have great potential of applications to low cost electronic devices and their circuits. Most organic compounds examined so far showed rather low field effect mobilities in the range of 10^{-5} –10^{-3} cm^2/Vs. Thin films of pentacene and polythiophene are known to exhibit high mobilities and received a considerable attention.

Drift mobility of single crystals and thin films of organic semiconductors have long been investigated with a time of flight method. The components of charge transfer complexes such as tetrathiafulvalene (TTF)- and tetracyanoquinodimethane (TCNQ)-based molecules are known to show high mobilities. The introduction of sulfur and selenium into a molecule by chemical synthesis makes it possible to have strong intermolecular interaction. Among these molecules, a single crystal of bis-(1, 2, 5-thiadiazolo)-*p*-quinobis(1, 3-dithiole) (BTQBT) shows rather high hall mobility, that is 2.4–4 cm^2/Vs at room temperature. We have prepared and characterized thin film field effect transistors (FETs) of BTQBT and its derivatives. Preparation and characterization of the films were carried out under ultrahigh vacuum condition. Most materials examined showed *p*-type semiconducting behaviors. Among *p*-type molecules, BTQBT films deposited at room temperature showed *p*-type semiconducting behaviors with mobility of 0.1 cm^2/Vs. The on/off drain current ratio was 10^7. The mobility and on/off ratio reached to 0.2 cm^2/Vs and 10^8, respectively, by optimizing the film growth conditions. These performances are almost comparable to those of pentacene and polythiophene thin films, indicated that BTQBT molecule is a prominent semiconducting material as a high mobility thin film. It was also found that tetracyanoquinodimethane (TCNQ) derivative showed an *n*-type semiconducting behavior with an electron mobility of 8.9×10^{-4} cm^2/Vs.

Generation of Reactive Species *via* Electron Transfer on Metal Complexes, as Basis of Chemical Energy Conversion Systems

NAGATA, Toshi; HINO, Takami; ITO, Hajime; KIKUZAWA, Yoshihiro

This project aims at developing redox catalysis reactions suitable for chemical energy conversion. Our current interest focuses on modeling photosynthesis, that is, driving endothermic chemical transformation by using light energy via photoinduced electron transfer. Progress has been made in the following topics during the last year:

A. Examination of various terdentate ligands as candidates for new electrocatalysis. We found that replacing one or two pyridine rings in 2,2':6',2"-terpyridine (terpy) gives new, useful terdentate ligands. The ligands are prepared by two steps from easily obtained formylpyridine derivatives. The ruthenium (II) complex of the 6-(2-pyrrolyl)-2,2'-bipyridine derivative was prepared and characterized. The redox potential of the Ru(III)/-Ru(II) couple appeared 1.10 V more negative than the bis(terpyridine) complex, indicating that the higher oxidation states are more accesible for this complex.

B. Light-driven oxidation of alcohols by a TEMPO/-quinone/porphyrin system was investigated. Initial survey of the reaction conditions suggested that the reaction was initiated by photoinduced electron transfer from the porphyrin to the quinone.

Electronic Structures and Reactivities of Organic/Metal Clusters

NEGISHI, Yuichi; SAKURAI, Hidehiro[1]; MURAYAMA, Haruno; TSUKUDA, Tatsuya
([1]Osaka Univ.)

Metal clusters stabilized by organic molecules exhibit novel catalytic properties due to the unique geometric and electronic properties of the metallic cores and tailor-made functions of the organic molecules. However, the fabrication of the organic/metal clusters as catalysts is not trivial; stabilization by organic molecules, which is inherent to hinder coalescence of the clusters, reduces the catalytic activities of the clusters. In order to tackle such dilemma, we have employed various reagents to stabilize the clusters with minimal extent of surface poisoning. The molecules we used are dendrimers and thiol molecules with bulky functional group or cyclodextrins. The organic/metal clusters were prepared by chemical reduction of the relevant metal ions in the presence of these molecules. Geometric structures of the clusters were studied by mass spectrometry, TEM, and, EXAFS measurements. In this project, we aimed to reveal the correlations between the chemical reactivities and the electronic structures of the clusters studied by photoelectron spectroscopies.

Local Distribution of Photoexcited States on a Semiconductor Surface as Observed by Scanning Tunneling Spectroscopy

KOMIYAMA, Masaharu; GU, Ning[1]; LI, Yanjun; MATSUMOTO, Taki
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The photocatalytic processes occurring on a semiconductor catalyst surface may be divided into two parts: physical processes that are initiated by photoexcitation of titania electrons, and following chemical processes which are the so-called heterogeneous catalysis. The former physical processes are commonly described within the framework of band model which assumes infinite array of three-dimensional (3-D) unit cells that give rise to a periodic potential, with which the electronic band structure is defined. Thus upon UV light illumination electrons in the valence band of titania are excited to its conduction band, leaving holes in the valence band, and they migrate within each band following the energy gradient until they annihilate each other, trapped in some (defect) sites, or consumed by subsequent chemical processes. However, at the solid surfaces and in superfine particles which are the common forms of practical photocatalysts, this infinite array of unit cells in three dimensions no longer exist, and their electronic band structure are known to be quite different from that of bulk.

This very surface is where the chemical part, namely heterogeneous catalysis, occurs. It is a highly local process: individual reactant molecules adsorb on a solid catalyst surface, react in one or more steps, and the product molecules leave the surface in the process called desorption. The adsorption and/or reaction sites in heterogeneous catalysis are often very specific, in terms of their atomic and/or electronic configuration: some reactant may need particular arrangements of atoms that is present on the catalyst surface, and others may need particular electronic states of the surface atoms to provide unique adsorption or reaction sites.

Despite these vastly different descriptions between the two processes occurring in heterogeneous photocatalysis, namely the physical process that is described by infinite 3-D or 2-D array of unit cells, and the chemical process that necessitates very local description of catalyst surface, no efforts to bridge this gap are known to the authors. The present work is the first of such attempts, and examines the local electronic characters of titania surface upon UV-light illumination by means of scanning tunneling microscopy (STM).

On a single crystal titania with its (110) surface polished, we found a structure that respond to UV light irradiation.[1)] It was an area where there exist two islands connected by a narrow bridge whose width is about 2.5 nm. When the UV light is turned on, this bridge becomes brighter, and then goes back to the original brightness when the light is turned off. This brightness change of the bridge can be reversibly repeated. The interpretation of above results is in progress, and also an effort to detect the same effect at atomic level is in progress.

Reference

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Electronic Structures and Surface Molecular Orientation of Organic Thin Films and Interfaces by Various Surface Sensitive Spectroscopies

OKUDAIRA K., Koji

Molecular orientation at the surface of organic thin films has recently gained considerable attention, since it affects electronic and optical properties of organic devices. Thin films of pendant group polymers are the most promising candidates for practical use due to their stability and facility of preparation. Furthermore, their surface properties can be easily controlled by changing the pendant chemical group. However, in general the molecules in polymer solids are not ordered due to the large molecular-weight distribution and mixed tacticy, *etc.*, and therefore it is believed that the pendant groups are also unoriented at the surface. Furthermore, since the properties of organic devices consisting of the films depend strongly on the molecular orientation at the film surfaces, determination of the surface molecular orientation such as tilt angle distribution of pendant group is very important for understanding the device properties.

The molecular orientation at the surfaces of poly(9-vinylcarbazole) (PvCz) thin films was studied by angle-resolved ultraviolet photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy using synchrotron radiation. The observed take-off angle (θ) dependence of photoelectron intensities from top π band peaks clearly at larger θ than the calculated one for the three-dimensional isotropic random orientation model. The results indicate that there are more pendant groups with large tilt angles than the three-dimensional isotropic random orientation model, which is in good agreement with the result obtained from NEXAFS spectroscopy. The surface electronic states of PvCz may be rather dominated by σ(C–H) states at the pendant carbazole group than π states.

Development of “Entropy-Saving” Nano-Materials

OBA, Toru; MINABE, Masahiro[1]
([1]Utsunomiya Univ.)

Development and arrangement of molecular devices have been highlighted for downsizing and energy-saving in electronics and photonics. For global, sustainable development, in our opinion, such future materials should also be “entropy-saving”: reusable, repairable, and bio-degradable. For development of the material system that is endowed not only with a structural order at the nano- and molecular-scale but with energy- and entropy-saving properties, we have fabricated new concept devices that utilize molecular self-assembly. The device is operated simply by mixing the functional blocks and switching external stimuli. This device, that functions only in the assembled state, can easily be decomposed into the components on demand, and the components can readily reassemble on demand to recover the function again. Exchangeability of the building blocks facilitates repair of damaged blocks, change of the function of the device, and integration of plural functions. The present study should serve a new design principle for intelligent nano-materials (see VIII-S).

Investigation of Dynamics on Photo-Excited Solids and Surfaces by Using the Combination of Synchrotron Radiation and Laser Light

KAMADA, Masao; TAKAHASHI, Kazutoshi

Dynamics on solids and surfaces excited by photons has attracted much interest from both of basic and application sides, since it may provide new scientific fields and photo-controllable devices. We have been investigating the photo-induced phase transition using photoelectron spectroscopy based on the combination of synchrotron radiation and laser light. Core-level and valence-band photoelectron spectra of organo-metalic complex showed clearly the characteristics of the photo-induced phase transition. We have been also investigating the photo-induced phenomena on semiconductor surfaces using the combination of synchrotron radiation and laser light. Photo-induced core-level shifts observed on GaAs(100) can be interpreted in terms of surface photo-voltage effects. This work has been extended to the super-lattice systems and another semiconductors and also to the investigation of the dynamics using the experimental system for the time-response on the semiconductor surfaces. We have also conducted the two-photon excitation experiments using synchrotron radiation and laser light to understand the details of the excitonic processes in condensed matters.

Construction and Commissioning of In-Vacuum Undulator

KATOH, Masahiro; HAYASHI, Kenji; HORI, Yoichiro[1]; HOSAKA, Masahito; KINOSHITA, Toshio; TAKASHIMA, Yoshifumi; YAMAZAKI, Jun-ichiro; KITAMURA, Hideo[2]; HARA, Toru[2]; TANAKA, Takashi[2]
([1]IMS and KEK-PF; [2]RIKEN)

We have completed the construction of an in-vacuum undulator for UVSOR-BL7A until February 2002. The overall length is 1.4 m. The period length is 36 mm and the number of periods is 26. The undulator was successfully installed in the storage ring during the spring shut down as shown in Figure 1. The performance test is in progress. It has been shown that the magnetic gap could be narrowed as small as 18 mm without reducing the beam lifetime. We have not observed any heat problem nor beam instability. The synchrotron radiation spectra will be measured in this autumn.

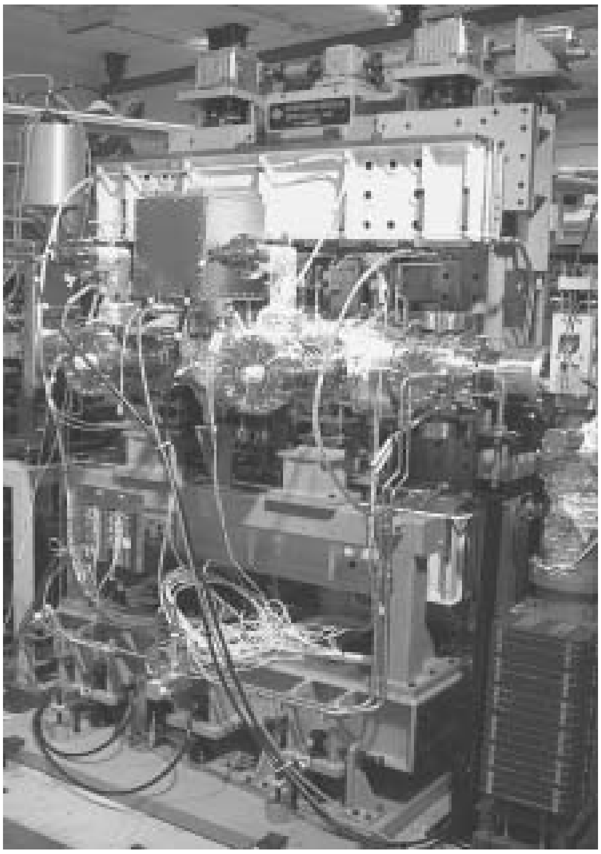

Figure 1. In-vacuum Undulator at UVSOR BL7A.

Optical Investigation on Fermiology of Strongly Correlated Electron Systems

KIMURA, Shin-ichi

Strongly correlated electron systems attract much attention because of their various physical properties. Since the origin is the interaction between the carriers and the localized magnetic moments, we are investigating the electronic structure near the Fermi level (Fermiology) by infrared and photoemission spectroscopies using synchrotron radiation. In this year, we measured optical reflectivity spectra of $Yb_4(As_{1-x}Xp_x)_3$ (Xp = P, Sb), $CeSbNi_{0.15}$, $Yb_{1-x}Lu_xB_{12}$, infrared magneto-optical spectra of $Ce_{1-x}La_xSb$, $Tl_2Mn_2O_7$, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ and resonant photoemission spectrum of $EuNi_2(Si_{0.25}Ge_{0.75})_2$. Now we are constructing a high energy resolution angle-resolved photoemission apparatus installed at BL5A of UVSOR. The apparatus will become a powerful tool for the investigation of the Fermiology of strongly correlated electron systems including organic conductors.

Preparation of Artificial Metalloenzymes by Insertion of Chromium(III) Schiff Base Complexes into Apo-Myoglobin Mutants

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Construction of artificial metalloenzymes is one of the most important subjects in bioinorganic chemistry, because metalloenzymes catalyze chemical transformation with high selectivity and reactivity under mild conditions. In this project, we have taken a novel strategy for the preparation of artificial metalloenzymes by noncovalent insertion of metal complex catalysts into protein cavities. Manganese(III) and chromium(III) Schiff base complexes are known as catalysts for various oxidations in organic solvents, thus, [M$^{\mathrm{III}}$-(salophen)]$^+$ [**M·1**, M = Mn and Cr, salophen (**1**) = N,-N'-bis(salicylidene)-1,2-phenylenediamine], are employed to insert into a chiral cavity of apo-Mb. For the creation of artificial metalloenzymes, apo-Mb is an excellent candidate since reconstitution of apo-Mb with heme has been well studied. The reconstitution of apo-Mb mutants with Cr(salophen) was carried out by applying a method for modified hemes. The H_2O_2-dependent sulfoxidation of thioanisole was examined by Cr(salophen)·apo-Mb mutants and Cr(salophen)·apo-H64D/A71GMb exhibited the highest sulfoxidation activity and Cr(salophen)·apo-H64DMb was the lowest. Figure 1 shows a preliminary crystal strucure of Cr-(salophen)·apo-A71GMb.

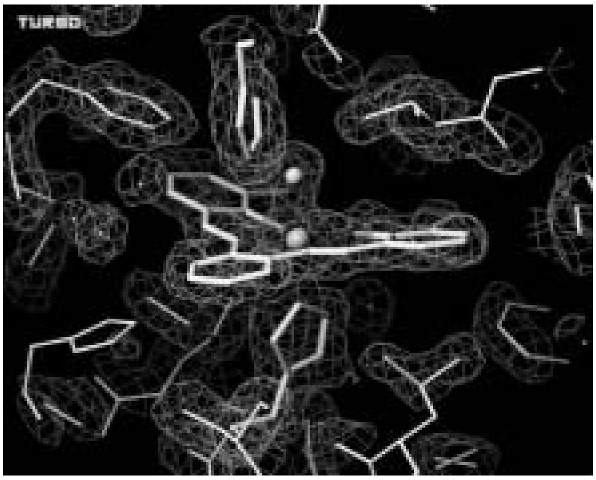

Figure 1. Preliminary crystal strucure of Cr(salophen)•apo-A71GMb.

Molecular Mechanism of Oxygen Activation by Metalloenzymes

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Metalloenzymes are a class of biologically important macromolecules that have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloenzymes have been thought to depend on the coordination structure of the active site in the protein matrices; the ligand donors, the geometry, and the coordination mode of reactant and substrate. Furthermore, it has been thought that protein structures in immediate vicinity of active metal ion are related to enzymatic function, regio-selectivity, and stereo-selectivity. In this project, we are studying the molecular mechanism of activation of molecular oxygen mediated by metalloenzymes.

(1) To understand the structure-function relationship of 3,4-PCD, there have been attempted over several decades to prepare inorganic model complexes that mimic the ferric iron site of 3,4-PCD, however, no ferric iron complex with the same coordination structure that in the enzyme has been characterized definitively. We have succeeded in an attainment to the ferric iron active site of 3,4-PCD by using sterically hindered salen ligand. Characterization of the model complex revealed the roles of the iron bound water ligand in the enzyme on the unique trigonal bipyramidal structure and the catechol degradation reaction.

(2) Small molecule axial ligands potentially can serve as useful NMR probes for characterization of environment and electronic structure of prosthetic group in heme protein. In this regard, the diamagnetic ferrous states have been examined thoroughly because of easy signal detection from iron bound small molecule. We reported the first detection of ^{13}C-NMR signal of the iron bound ^{13}CN in heme proteins such as sperum whale myoglobin(Mb), human hemoglobin(Hb), horse heart cytochrome *c*(Cyt-*c*), and horseradish peroxidase(HRP). This study showed that the ^{13}C-NMR spectroscopy of the iron bound ^{13}CN provides a probe for studying nature of the proximal ligand in ferric heme protein.

(3) Heme oxygenase (HO) catalyzes the O_2- and NADPH-cytochrome P450 reductase-dependent conversion of heme to biliverdin and CO through a process in which the heme participates both as prosthetic group and substrate. To investigate the functionality of highly conserved polar amino acids in the distal helix of HO-1, we have generated a detailed reaction cycles for the first mono-oxygenation step of HO catalysis. We employed EPR and ^{1}H, ^{14}N ENDOR spectroscopies to charcterize the intermediates generated by 77 K radiolytic cryoreduction and subsequent annealing of wild-type oxy-HO and D140A, F mutants.